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UTILIZATION OF COAL FLY ASH

BY

SUSANNE C. OPENSHAW

A REPORT PRESENTED TO THE GRADUATE COMMITTEE
OF THE DEPARTMENTS OF ENVIRONMENTAL ENGINEERING AND
CIVIL ENGINEERING IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF ENGINEERING

UNIVERSITY OF FLORIDA, Gainesville,
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LIST OF ABBREVIATIONS

Al	Aluminum	Sr	Strontium
As	Arsenic	Th	Thorium
B	Boron	Ti	Titanium
Ba	Barium	Tl	Thallium
Br	Bromine	U	Uranium
C	Carbon	V	Vanadium
Ca	Calcium	W	Tungsten
Cd	Cadmium	Zn	Zinc
Ce	Cerium		
Cl	Chlorine		
Co	Cobalt		
Cr	Chromium		
Cu	Copper		
Eu	Europium		
F	Flourine		
Fe	Iron		
Ga	Gallium		
Hg	Mercury		
I	Iodine		
In	Indium		
K	Potassium		
Mg	Magnesium		
Mn	Manganese		
Mo	Molybdenum		
Na	Sodium		
Ni	Nickel		
P	Phosphorus		
Pb	Lead		
Po	Polonium		
Rb	Rubidium		
S	Sulfur		
Sb	Antimony		
Sc	Scandium		
Se	Selenium		
Si	Silicon		

KEY WORDS

Coal
Fly Ash
Environmental Impacts
Metals
Construction
Concrete

ABSTRACT

Coal-fired power plants produce approximately 80 million tons of fly ash each year. Efforts to use fly ash have reached only a twenty to thirty percent reutilization rate. A literature review was performed to provide a consensus of the available information regarding fly ash. Fly ash is highly variable depending on the coal source, plant operations, and several other parameters. The various fly ash characteristics are discussed including classifications, physical characteristics, chemical properties and chemical compositions. Although extensive research has been performed on the use of fly ash, very little of this research has monitored any environmental impacts. The environmental concerns addressed include mobilization of toxic elements, biota impact, microbial impact, handling dangers, and pertinent regulations. Finally, the various disposal and reutilization options for fly ash are examined. A recommendation is provided for further research to cover deficiencies found in the literature.

EXECUTIVE SUMMARY

Coal-fired power plants produce approximately 80 million tons of fly ash each year. Fly ash is exempt from handling as a hazardous waste by the Resource Conservation and Recovery Act (1976), Subtitle C, Section 3001. In spite of this status, only twenty to thirty percent of fly ash is presently reused. Speculation is made that the cause for the low reutilization rate is concern regarding adverse environmental effects. Limited research has been accomplished in this area. A literature review was performed to collect available information regarding fly ash characteristics, environmental concerns and options.

Fly ash characteristics are an important precursor to understanding the reactions in field conditions. There is no single standard classification system for fly ash, however, most schemes stem from the difference in the eastern and western coals. Since fly ash is the portion of the ash that is small enough to be carried away from the boiler in the flue gas, it is understandable that the majority of the particles are 2 - 20 μm in diameter, a medium to fine silt range. The fly ash morphology is usually characterized as spherical nonopaque particles with a surface area range of about $1 \text{ m}^2/\text{g}$. Permeability of fly varies significantly (1×10^{-6} to $8 \times 10^{-4} \text{ cm/sec}$) depending on compaction. A low permeability is often desirable. Similarly, density varies with compaction.

Chemical properties and composition provide the greatest variability to fly ash. Eastern fly ash has a pH near 4 whereas western fly ash tends to have a pH range from 8 - 12. An acidic pH tends to discourage leaching of certain components. The primary elements of concern in leachate are usually As, Se, and B. Radioactivity of fly ash oscillates close to the level of concern at 5 pCi/g ^{225}Ra . Fly ash is composed of a variety of elements such as (in order of decreasing abundance): Si, Al, Fe, Ca, C, Mg, K, Na, S, Ti, P, and Mn. Most of the major elements are in the stable core, but trace elements on the surface can cause the most problems. The major constituents in fly ash are SiO_2 , Al_2O_3 , Fe_2O_3 , and CaO . The predominant mineralogy for fly ash is amorphous glass which is important since it gives fly ash its pozzolanic properties.

The primary environmental concern is the mobilization of toxic elements. Initial research indicates levels of elements in leachate are below the enforcement standards. However, there has been limited research outside the laboratory to verify this. The primary concerns with the impact on biota appear to be the toxic effects of high levels of Boron to plants, and animals eating plants grown on fly

ash amended soils with high levels of Selenium. Fly ash has also been found to impair the microbial population.

The options for fly ash include disposal or reutilization. The two methods of disposal include dry disposal or wet-sludging. Many reutilization options have been investigated, but today the most popular method is fly ash in concrete. Structural fills or embankments have the most potential for high volume use of fly ash, although, again, minimal research has been done in this area. Incorporation of fly ash into a roadway base or subbase is potentially a good use for fly ash. Other areas briefly reviewed include soil amendment, mineral resource, underwater construction, and various other preliminary studies.

The limiting factor for any fly ash option is the lack of environmental research performed for field conditions. A recommendation is provided for further research to cover deficiencies found in the literature.

1.0 INTRODUCTION

Coal-fired power plants produce large quantities of combustion residue each year. The solid waste residue includes bottom ash, slag and fly ash. Fly ash is the portion of residue that has sufficiently small enough particle size to be carried away from the boiler in the flue gas. Fly ash accounts for approximately seventy percent of the solid waste produced from coal combustion (Roy *et al.*, 1981; Cheremisinoff, 1988). The generation of coal fly ash has steadily increased in each of the last fifteen years:

1976 - 36 m tons	(Theis and Wirth, 1977)
1977 - 48 m tons	(Roy <i>et al.</i> , 1981)
1980 - 56 m tons	(Spencer and Drake, 1987)
1990 - 80 m tons	(Stoewsand <i>et al.</i> , 1990)

In comparison to other ashes produced in 1990 (4 m tons municipal solid waste and 1 m tons wastewater sludge ashes), coal fly ash creates a significantly larger scale disposal problem (Theis and Gardner, 1990).

Environmental impacts from fly ash disposal, recycling, and reuse have only recently become identified as an important topic of research. Europe is reusing forty to fifty percent of their coal fly ash (Adriano *et al.*, 1980) and Japan is reusing sixty percent (Wong and Wong, 1989), whereas the United States has consistently reused only twenty to thirty percent (Chang *et al.*, 1977; Theis and Gardner, 1990; Sandhu and Mills, 1991). Although many fly ash reutilization projects have been performed with positive results, most are still perceived as experimental primarily due to the environmental implications. A thorough knowledge of the physical characteristics, chemical composition, and properties is essential to understanding any possible environmental impacts. Once the environmental impacts can be confidently predicted, a larger market can be encouraged to productively reuse fly ash.

This paper provides a current, thorough literature review that describes the characteristics of fly ash, environmental concerns, and existing methods of handling fly ash. A recommendation for the best use of fly ash accompanied by suggestions for further research is also provided. It should be noted at this point that an extensive literature review was performed by Roy *et al.* (1981) for pertinent literature through September 1980. Information from that review will be noted, but the emphasis will be on literature published since 1980.

2.0 FLY ASH CHARACTERISTICS

The properties of fly ash vary from one sample to the next depending on the source of the coal; degree of coal preparation, cleaning and pulverization; design, type and operation of the power plant boiler unit; conditions during combustion; additives used to assist combustion or improve precipitation performance; efficiency of emission control devices; storage and handling of the byproducts; and the prevailing climate (Adriano et al., 1988; EPRI, 1992).

Several methods are used by the power plants to collect fly ash. They include one or more of the following particulate control devices: wet scrubbers, mechanical collectors, fabric filters, and electrostatic precipitators (EPRI, 1992). Each method has its own advantages and disadvantages, but aside from some gradation differences, the fly ash is not affected by the collection device.

Coal used in the United States can be divided into two major categories: eastern coals and western coals. Eastern coals are anthracite and bituminous coals. They are normally high in Fe which accounts for the reddish or brownish colored fly ash. The western coals are subbituminous and lignite coals. They have higher pHs and higher levels of B, Ca, Mg, and Na than the eastern coals (El-Mogazi et al., 1988). The fly ash from western coal is usually dark or light grey with some samples white or cream colored.

A summary of the various classifications, physical characteristics, chemical compositions and chemical properties is provided. Due to the diversity of fly ashes, full characterization should be performed on the particular fly ash to be used in a project.

2.1 CLASSIFICATION OF FLY ASH

Various classification schemes have been proposed to organize fly ashes. Each scheme originated with a different purpose in mind. Two methods were designed to identify the suitability of fly ashes as pozzolanic and cementitious materials (Mattigod et al., 1990). A system proposed by the United States Environmental Protection Agency (USEPA) evaluates the disposable solid wastes according to the risk of mobilization of potentially toxic constituents (based on extraction concentration of certain elements). Roy et al.(1981) and Roy and

Griffin (1982) proposed a classification system based on chemical composition, hydration pH, and particle size distribution. The only method repetitively referred to in literature is a method developed by the American Society for Testing and Materials (ASTM). This method is based on the source of coal and specified major element oxide content (Mattigod *et al.*, 1990). The two types classified are Type F and Type C fly ash. Type F comes predominantly from burning eastern coal and must contain at least seventy percent of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$. Type C fly ash is from western coal and must have a minimum of fifty percent $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$. Type C has a higher calcium content which exhibits self hardening or rapid setup when mixed with water (Collins, 1988).

2.2 PHYSICAL CHARACTERISTICS

Although fly ash does vary from sample to sample, some generalizations can be made. The size distribution, morphology, surface area, hydraulic conductivity or permeability and density are reviewed.

2.2.1 Size Distribution

Fly ash is the portion of combustion solid waste residue with small enough particle size to be carried away in the flue gas. Eighty to 99 percent of a fly ash sample by weight passes a No. 200 sieve, which has a 0.074 mm (74 μm) screen size. Under the Unified Soil Classification System a soil is described as "fine grained" if more than half by weight passes the No. 200 sieve. Fly ash is generally fine grained and falls within the silt range (2 μm to 74 μm) (Martin *et al.*, 1990). The literature was consistent in reporting the particle diameters:

Mattigod <i>et al.</i> , 1990	20	-	80	μm	avg range
Fisher <i>et al.</i> , 1978	0.8	-	20	μm	avg range
Theis and Gardner, 1990	10	-	125	μm	avg range
Roy <i>et al.</i> , 1981		<	10	μm	65-90%
Spencer and Drake, 1987		>	50	μm	21-25%
	2	-	75	μm	70-73%
		<	2	μm	5-7 %
Chang <i>et al.</i> , 1977		>	50	μm	33 %
(most frequently cited study)	2	-	50	μm	63 %
		<	2	μm	4 %

It can be concluded that the majority of the particles are in the medium to fine silt range (2-20 μm).

Although literature seldom indicated which method was used to discover particle size, Fisher *et al.* (1978) describes three different methods: count median diameter (CMD) determined from scanning electron micrographs, volume median diameter (VMD) determined by Coulter analysis, and mass median diameter (MMD) determined from Stokes' law of settling in aqueous dispersion. Text books for Soil Mechanics refer to the hydrometer test which is a method using Stokes's law (Lambe and Whitman, 1969; McCarthy, 1982).

The gradation of the fly ash can be determined by calculating the uniformity coefficient (C_u) of a sample. This is found by determining the particle diameter where sixty percent of the fly ash sample weight is finer (d_{60}) and dividing by the particle diameter where ten percent is finer by weight (d_{10}). If this value is less than two, it is considered very uniform; if it approaches ten, it is considered well-graded (Lambe and Whitman, 1969). Mattigod *et al.* (1990) report a range of 2.0 to 9.8. Another study of five fly ash samples revealed values ranging from 2.4 to 9.0, but with an average of four (Martin *et al.*, 1990). The difference in results could be accounted for by the collection device. The electrostatic precipitator or wet scrubber fly ash will have similar gradation, whereas the mechanical cyclone collector fly ash has a coarser gradation. Disregarding any cementitious properties, a well-graded soil experiences less breakdown than a uniform soil of the same particle size, since the well-graded soil has many interparticle contacts and the load per contact is thus less than in the uniform soil (Lambe and Whitman, 1969).

The size of the particle appears to have an effect on the concentration of elements. The volatilization of certain elements causes a concentration increase as the particle size decreases. The elements found to have varying levels of enrichment in smaller particles are (in alphabetical order): As, B, Ba, Br, Cd, Cl, Co, Cu, Cr, Fe, Ga, Hg, I, In, Mg, Mn, Mo, Ni, Pb, Po, Rb, S, Sb, Sc, Se, Sr, Tl, W, V, and Zn (Roy *et al.*, 1981). The chemical composition of fly ash is discussed further in section 2.3.

2.2.2 Morphology

The morphology of a fly ash particle is defined as the form or structure of the particle. Knowing the particle morphology can be helpful to understanding the physical properties and leaching behavior of the fly ash. Fisher *et al.* (1978) defined eleven major morphological classes with the use of light microscopy. The classes were based on opacity, shape, and types of inclusions. The classes are as follows:

- A) Amorphous, nonopaque
- B) Amorphous, opaque
- C) Amorphous, mixed nonopaque and opaque
- D) Rounded, vesicular, nonopaque
- E) Rounded, vesicular, mixed nonopaque and opaque
- F) Angular, lacy, opaque
- G) Cenosphere (hollow sphere), nonopaque
- H) Plerosphere (sphere packed with other spheres), nonopaque
- I) Solid sphere, nonopaque
- J) Sphere, opaque
- K) Sphere with either surface or internal crystals, nonopaque

Fly ash has a very high percentage (67 to 95 percent) of spherical nonopaque particles (class G and I) (Fisher *et al.*, 1978). Class G dominates for particles 20 - 74 μm in diameter, and class I for particles less than 10 μm (Roy *et al.*, 1981). Fisher *et al.* (1978) indicate the particle composition (ie. iron oxides content) contributes to the level of opaqueness, whereas the combustion exposure time and temperature are responsible for the different shape characteristics. It is their theory that as the coal is exposed to the combustion temperature, the resulting fly ash changes shapes from amorphous to rounded vesicular to lacy and finally spherical.

Tazaki *et al.* (1989) similarly concluded the morphology is acquired during cooling of the non-combustible mineral content of the original coal while being carried along with the liquid-gaseous combustion products on or near the surface phase, or around the nucleus.

Wadge *et al.* (1986) suggest the pulverization process which reduces particles to less than 100 μm diameter before combustion contributes to the resulting spherical shape. The combustion chamber operates at approximately 1500° C which allows the particles to be fused and condense into cenosphere shapes as a result of surface tensions (Wadge *et al.*, 1986).

Almost all literature reviewed cite one of Fisher's works with regard to determining the morphology (Mattigod *et al.*, 1990; El-Mogazi *et al.*, 1988; Cherry *et al.*, 1987; Wadge *et al.*, 1986; Tazaki *et al.*, 1989; Spencer and Drake, 1987; Schure *et al.*, 1985; Roy *et al.*, 1981). However, most authors referred to the solid sphere (class I) as a plerosphere (class H). Differentiation between class H and class I appears to be difficult.

It should be stressed that similar morphologies do not necessarily indicate equivalent chemical composition. However, as Fisher *et al.* (1978) indicate, it is possible that a particular morphology of fly ash will possess a greater toxicity and should, therefore, be carefully controlled.

2.2.3 Surface Area

The surface area of particles is important because it may control the total adsorption capacity (although not necessarily the desorption rate). The surface areas of fly ash particles generally vary inversely with the particle size (ie. the smaller the particle, the larger the surface area). Schure *et al.* (1985) performed a series of tests determining the surface area and porosity of western coal fly ash. They found, for the 0 - 74 μm particle size range, the surface area did in fact decrease with increasing particle size. However, for particles over 74 μm the shape deviates from the spherical shape and forms irregular sponge like shapes which in turn increases the surface area. The larger particle sizes are usually carbonaceous which indicates they are likely the result of incomplete combustion.

El-Mogazi *et al.* (1988) found the surface areas range from 0.45 - 1.27 m^2/g . Mattigod *et al.* (1990) indicate a slightly wider range from 0.2 - 3.06 m^2/g . Theis and Gardner (1990) report unusually high surface areas with 1 - 9.44 m^2/g . However, they also reported a wide range of particle sizes (0.01 - 125 μm), probably indicating the samples were taken from different stages of combustion.

2.2.4 Permeability/Hydraulic Conductivity

Permeability and Hydraulic Conductivity (K) are terms that are often used interchangeably for the same property. It appears hydrologists and physicists use the term hydraulic conductivity whereas geotechnical engineers use coefficient of permeability. Both terms will be used as referenced in the literature. However, coefficient of permeability (L/T) should not be confused with intrinsic permeability (L^2). The coefficient of permeability or hydraulic conductivity (K) take into account the fluid properties and the medium properties, whereas intrinsic permeability (k) only refers to the effectiveness of the porous medium alone (Gupta, 1989). They are related by the following equation:

$$K = k\gamma/\mu$$

where γ = specific weight of fluid, and

μ = dynamic viscosity of fluid.

Permeability (K) is defined as a measure of the amount of fluid that will flow through a sample for a given time without causing displacement (Lambe and Whitman, 1969). It should be noted that the fluid is actually flowing through the void spaces, not the particulate matter. Therefore, porosity can have a controlling influence on permeability (Freeze and Cherry, 1979).

Porosity is a value that portrays the amount of voids in a sample which is representative of the water bearing capacity (Gupta, 1989). Porosity is usually

represented by η . It is determined by calculating the ratio of the volume of the voids to the total volume (multiply by 100 to express as percent). Obviously the porosity and therefore permeability can be affected by compaction (density) since this reduces the amount of void space for a given total volume. Normally the higher porosity samples will have a higher hydraulic conductivity (although this is not necessarily true for all types of soils) (Freeze and Cherry, 1979).

Fly ash compacted in a laboratory to 95 percent maximum density can achieve a permeability of 1×10^{-5} cm/sec (Peffer, 1982). A higher density results in a lower permeability. This is beneficial since a low permeability will restrict leachate from migrating away from the site. Similar results were found in other studies: a compacted fly ash generally has a low hydraulic conductivity at 9 cm/day (1×10^{-4} cm/sec), whereas uncompacted fly ash can be as high as 70 cm/day (8.1×10^{-4} cm/sec)(Roy *et al.*, 1981; Cheremisinoff, 1988).

A study by Martin *et al.* (1990) of compacted fly ash samples revealed permeabilities ranging from 1.2×10^{-4} to 1.8×10^{-5} cm/sec. They also cited a previous study of forty-one samples with a mean saturated permeability of 1.3×10^{-5} cm/sec with a standard deviation equal to a half order of magnitude.

Goodwin (1988) reported slightly lower permeabilities with values of 1×10^{-5} to 1×10^{-6} cm/sec. Turgeon (1988) reported a very densely compacted Pittsburgh fly ash with a permeability of 5×10^{-5} cm/sec. These ranges approach the limit many regulatory agencies have set for secondary liners (1×10^{-7} cm/sec) (Usmen *et al.*, 1988).

EPRI (1992) indicates the type of feed coal has an impact on the permeabilities as indicated below:

Bituminous	1×10^{-4} to 1×10^{-7} cm/sec
Subbituminous	1×10^{-5} to 3×10^{-6} cm/sec
Lignite	9×10^{-6} to 1×10^{-7} cm/sec.

When fly ash was used to amend soil for plant growth, the hydraulic conductivity in the soil increased until the fly ash accounted for 10 to 20 percent by volume (Adriano *et al.*, 1980; Chang *et al.*, 1977; Golden, 1983). Once this point was reached, the hydraulic conductivity decreased. This seems to be a result of the fly ash's pozzolanic reaction which tends to cement when in contact with water. A smaller amount of fly ash is needed in acidic soils to reach this turning point (Adriano *et al.*, 1980).

The low hydraulic conductivity can be very desirable if the fly ash is to be reused. Even in a disposal situation, a low hydraulic conductivity would

discourage water from seeping through and forming leachate, especially if a higher hydraulic conductivity layer surrounds the fly ash (path of lower resistance).

2.2.5 Density

Density is defined as mass per unit volume. Again, density is also affected by compaction. In a laboratory test of eastern bituminous coal fly ash, a 95 percent maximum density of 1.3 g/cm³ was achieved (Peffer, 1982). The disposed state was 85 percent maximum density with a 1.1 g/cm³ density. Other reports support this finding:

Theis and Gardner (1990)	1.12 - 1.28 g/cm ³
Mattigod <u>et al.</u> (1990)	1.01 - 1.43 g/cm ³
Martin <u>et al.</u> (1990)	1.02 - 1.42 g/cm ³

Turgeon (1988) indicated a high density of 1.52 - 1.60 g/cm³. Schure et al. (1985) reported particle densities for various sizes at a range of 1.91 - 1.97 g/cm³, but with a 2.24 g/cm³ spike for 10 - 20 μm particle sizes.

Since fly ash generally has a low bulk density, fly ash addition to soil reduces the bulk density of soil (Adriano et al., 1980; Chang et al., 1977). This will be discussed further in Section 3.2.1.1.

2.3 CHEMICAL PROPERTIES

2.3.1 pH

The pH of fly ash varies depending on the source of the coal. Fly ash is known to be both acidic and alkaline. Eastern bituminous coal fly ash has been measured to have a pH of 4.3 - 4.9 (Peffer, 1982). As noted previously the western coal fly ash tends to have higher pHs (ie. 8.16 - 12.4 (Theis and Gardner, 1990). The literature does not often report the actual pH of the fly ash (usually it is just noted that it is either acidic or alkaline), but most often the pH of the fly ash media is recorded.

El-Mogazi et al. (1988) found the fly ash pH affects the soil media. An alkaline fly ash used for amending soil increases the pH of the soil sample.

Fly ash has a very strong effect on the pH in an aquatic environment. The properties that appear to be the most responsible are the oxalate extractable iron (acid component) and water soluble calcium (basic component)(Theis and Wirth,

1977). Research performed by Theis and Wirth (1977) shows that the pH appears to control the desorption of metals from the surface of the fly ash surfaces; desorption increases as the pH decreases. Hollis *et al.* (1988) also found this to be true. Boron concentration in solution increased 100 times by changing the pH from 12.5 to 7.0. This leads to the conclusion that there should be higher environmental concern for ashes that produce a low pH environment.

2.3.2 Solubility

Fly ash particles are essentially insoluble glasses. However, the enriched surface elements are soluble (Roy *et al.*, 1981). The composition of any leachate depends on the solubility of trace metals and other components. As noted previously, the desorption and therefore the solubility of most heavy metals (as cations) is low in basic environments (Spencer and Drake, 1987). This can be attributed to metals precipitating or adsorbing onto hydrous iron and aluminum oxides (Golden, 1983). Theis and Gardner (1990) concluded that pH values below 7 favored solubilization of trace cations and pH values above 7 favored trace anions (As, B, Cr, Mo, Se).

The results of solubility experiments seem to be largely dependent on the extraction procedures, such as the nature of the extractant, the ash-to-solution ratio, pH, number of extractions and length of extraction time (El-Mogazi *et al.*, 1988). Dreesen *et al.* (1979) performed solubility experiments that found the most soluble trace elements under alkaline conditions were Mo, F, Se, and B. They also found in acid solutions that the highly volatile elements from the combustion process (As, B, Cd, F, Mo, and Se) were most easily extracted. According to this study, the metallic nature of the element can be used to predict the solubility. Nonmetals and semimetals appear to be more soluble than metals.

Elements of concern (tested for in USEPA toxicity tests) that were not reported as soluble are Ag, Ba, Hg, and Pb. Consistently B has been found to be the most soluble element (El-Mogazi *et al.*, 1988; Roy *et al.*, 1984). Roy *et al.* (1984) report other studies which found Cd, Co, Mn, P, and Zn were fairly soluble in alkaline solution, and B, Ca, and SO₄ exceeded the water quality limits in acidic fly ash extractions. However, it is evident that each study seems to get slightly different results. In their conclusion, Roy *et al.* (1981) state,

It is difficult to make generalizations about the relative solubilities of the constituents in fly ash. Such generalizations are complicated by the variable nature of the solid waste. Leachates may vary greatly in pH, which in turn is the dominant factor controlling the solubility of many constituents. The data base for

relative solubilities is not adequate and can not be used as a basis for making detailed generalizations.

Studies referenced above published after Roy *et al.* (1981) have not improved the ability to make generalizations about solubility. With this in mind, the only "common thread" statement that can be made about solubility is that the elements that predominate on the surface layer exhibit substantial solubility.

2.3.3 Leachate

The key to potential hydrological impact is the collection of contaminants by water as it percolates through or over a material. This can be analyzed by performing leachate tests. As with solubility tests, different results are achieved using different testing procedures. Leachate is also highly variable as a result of the type of coal and plant processes. This makes characterizing leachate difficult. Column leachate tests performed for a site in Delaware resulted in initially high total dissolved solids (TDS) and high levels of Arsenic (As) and Selenium (Se) (Strauss, 1984).

Research by Ruane *et al.* (1983) found that coal fly ash leachate samples were highly variable, but were generally high in TDS, B, Fe, Ca, Al, and SO₄, and often exceeded the USEPA's drinking water quality levels (ie. cadmium, chromium, iron, manganese, lead, TDS and pH). The acidic ash produced a higher concentration of metals in the leachate than the alkaline ash. Mattigod *et al.*'s (1990) results support this information. Ca and S (as SO₄) were the major elements released and at a higher percentage for an acidic solution (5 to 10 percent vs. 13 to 26 percent).

Roy *et al.* (1981) reported that the leachability of certain elements (P, Fe, Al, B, K, and Ca) decreased as the material aged. It was also indicated that the rate of leaching was affected by the fly ash particle size, agitation of the mixture, pH, and temperature of the water. Again it was concluded that low pH encourages leaching of trace metals. However, As does not follow this generality; a high pH favors the extraction of arsenic. Roy *et al.* (1981) reported the relative concentrations of elements leached in comparison with the amount available from ash sluice water at various pH levels:

Alkaline: Se > B > Cr > Ni > Cu > Ba > As > Zn > Al

Neutral: B > Cd > As > Se > Zn > Ni > Mn > Cu > Ba

Acidic: B > > Zn > Ca, F > Na > Mg, Co > Ni, Sr > Be > Cu, Pb, Al > >
Si, Fe, K

The behavior of elements is consistent with the idea that the elements that are prevalent on the surface solubilize as they reach their chemical form or physical location conducive to leaching.

It is important to note that the model developed by Liem *et al.* (1983) to predict leachate characteristics predict that after ten years more than 90 percent of the As, Cd, Cr, Mo, Ni, Se, and Zn would remain in the deposit and not leach out. Theis and Gardner (1990) report the aqueous solubility of fly ash ranges from 0.5 to 3 percent on a total mass basis. The total amount of leachate released does not appear to be extensive. However, this must be accurately predicted and compared to the appropriate regulations.

2.3.4 Toxicity

It was noted previously that certain toxic heavy metals are discouraged from leaching in an alkaline solution. However, considering continual rainfall and percolation, is it possible for the solution to become less alkaline and begin leaching? This can be evaluated by the USEPA Extraction Procedure (EP) toxicity tests. This test evaluates the content of a leachate for certain trace metals with the pH held at a constant 4.9 to 5.2 level. However, some potentially hazardous trace elements (B, Co, Mn, Mo, and V) are not tested by this procedure (Roy *et al.*, 1981). The metals of concern, their Resource Conservation and Recovery Act (RCRA) limits, and five leachate sample levels are displayed in Table 1.

It is evident that the reported values for these metals are within RCRA limits by over an order of magnitude except Selenium, which is still within the limits. Although the metals are not at a toxic level, as defined by RCRA regulations, this does not mean the fly ash or leachate does not have any toxic effects. For example, a high pH, or increased TDS, or a bioaccumulation can have a toxic effect on some organisms. Additionally, as more proof to the variability of the fly ashes or leaching procedures, a study by Roy *et al.* (1984) found a high level of 1.38 ppm for Cadmium using the EP toxicity test. Each fly ash sample has its own characteristics and must be identified in the field and laboratory.

TABLE 1. Toxicity Levels, TCLP

	RCRA (ppm or mg/L)	A	B	C	D	E
Arsenic	5	0.073	0.035	0.01	0.03	0.38
Barium	100	0.23	0.5	0.3	0.1	0.25
Cadmium	1	0.01	0.01	0.037	0.001	0.019
Chromium	5	0.01	0.04	0.067	0.02	0.044
Lead	5	0.04	0.03	0.06	0.01	0.33
Mercury	.2	<0.001	<0.001	0.0003	0.001	--
Selenium	1	0.328	0.104	0.002	0.015	0.12
Silver	5	0.01	0.01	<0.01	<0.01	--

(40 CFR 261.24, 1990; Martin *et al.*, 1990; C,D,E - Roy *et al.*, 1981)

The speciation of elements could be very important to the toxicity. Certain forms of elements may be more toxic, mobile or biologically available. For example, the toxic form of As is the As(III) oxidation state. Most of the arsenic found in this form generally exists in very low concentrations over a wide range of pH. Fly ash extracts normally have most of the arsenic in the non-toxic form As(V) (El-Mogazi *et al.*, 1988). It is difficult to determine the speciation of all potentially toxic elements, but this information could provide an explanation for a toxicity difference between two fly ashes with the same concentrations.

2.3.5 Radioactivity

Presently, although RCRA does not provide guidelines for radioactivity, fly ash would be considered as radioactive waste if the average ^{226}Ra concentration exceeded 5 picocuries per gram (pCi/g), or if a leachate had 50 picocuries per liter of ^{226}Ra and ^{228}Ra combined (Roy *et al.*, 1981). Furr *et al.* (1977) performed gamma emission tests on twenty three fly ash samples. The samples ranged from 3.9 to 14.4 pCi/g above background with an average of 6.4 pCi/g (a differentiation of specific radionuclides was not made). EPRI (1992) cited two different studies of radioactivity in fly ash. The first sampled twelve fly ashes and found six with levels greater than 5 pCi/g but none higher than 10 pCi/g. The second study tested 69 samples and only found seven had values greater than 5 pCi/g with the highest being 7 pCi/g.

A high correlation between gamma radiation and the concentration of Th and particularly U in fly ash was determined by Furr *et al.* (1977). The presence of Th and U in the fly ash is directly related to their presence in the earth's crust (which create the background radioactivity). The elements are therefore present in the coal. During combustion the elements form insoluble and non-volatile compounds that pass on to the ash (Golden, 1983).

In contrast to Furr *et al.*'s (1977) study, Golden (1983) found that the level of radioactivity for both Uranium and Thorium was 3-5 pCi/g. He estimated the radiation dose from coal ash is equal to only 0.1% of the natural background radioactivity. Studies reported by Torrey (1978b) that tested various fly ash samples reported radioactivity concentration ranges from 1.0 to 4.3 pCi/g for ^{226}Ra , ^{228}Ra , ^{228}Th , and ^{232}Th individually.

Krieger and Jacobs (1978) reported that different concentration levels occur as a result of the source of the coal and the differences in mining and coal washing operations. The different radioactivities can also be attributed to the plant operation and possibly treatment after the mining.

Fly ash radioactivity is a concern when the fly ash is reused. For example, when coal fly ash has been incorporated into concrete products (ie. concrete blocks, floor slabs, etc.) a radiation emanation problem has developed in the past (Krieger and Jacobs, 1978).

It is apparent from the literature that there is a lesser concern over radioactivity than other potential environmental problems. Since there does not appear to have been much recent investigations regarding radioactivity, this may be rather improvident. However, a majority of the radioactivity appears to concentrate in the bottom ash (Torrey, 1978b), and most studies have emphasized the airborne radioactive emissions, not the fly ash itself. This should not be taken as an indication of an acceptable environmental area. Further study of the radioactivity is recommended to confirm or deny its significance.

2.4 CHEMICAL COMPOSITION

It is important to understand that the elemental composition of fly ash is highly variable. The variability is directly related to the source of the coal, its pretreatment, and the operation of the plant burning the coal. A general overview of the elements, constituents, mineralogy, and organic content is provided. It should be emphasized again that assumptions about a particular fly ash composition cannot be made from this summarization. Individual characterizations should be made for each source of fly ash to be used in a project.

2.4.1 Elemental Composition

2.4.1.1 Fly Ash

The chemical content of the fly ash core is nearly overshadowed by the importance of the enriched surface layer. The surface layer becomes enriched when the elements that volatilize during coal combustion condense on the fine fly ash particles as the temperature of the flue gas cools downstream in the combustion train. The particles have a large surface area in comparison to mass (Mattigod, 1990). As previously noted, the surface area increases as the particle size decreases. This contributes to the phenomena that the smaller particles contain unusually large surface concentrations of potentially toxic trace elements (Tazaki *et al.*, 1989). Spencer and Drake (1987) indicate the metal concentration in surface coatings can be up to two orders of magnitude greater than those in the parent coal. The surface layer is what appears to define most of the important characteristics. For example, as noted in the discussion on pH, the relative amounts of amorphous iron oxides and lime that predominate on the surface determine the ultimate acidic or basic character of fly ash in solution (Theis and Wirth, 1977).

The major elements (greater than one percent) in order of decreasing abundance are Si, Al, Fe, Ca, C, Mg, K, Na, S, Ti, P and Mn (with the exception of C, most commonly reported in their oxidized state; see Constituent Composition section). Most of these major elements exist in the core of the fly ash which is relatively stable. This is probably because they are not volatilized in the combustion process (El-Mogazi *et al.*, 1988).

Trace metals on the surface of particles are most available to release into the aqueous environments. A study performed by Theis and Wirth (1977) determined the degree of surface concentration for metals since the analysis method (oxalate and/or hydroxylamine washes) only made surface metals soluble. The results are shown in Table 2.

Another study performed by Wadge *et al.* (1986) with fly ash from England found Arsenic (As) and Selenium (Se) highly concentrated on the crust or surface but minimal enrichment for cadmium (Cd) and lead (Pb). Although the first two elements were highly concentrated in the fly ash, they propose that this is not necessarily the result of an enrichment process during combustion, but likely due to the fact that they started at a high concentration in the feed coal.

TABLE 2. Surface Concentrations of Trace Metals
(% of total)

Metal	Range	Average
Arsenic	65-100	93
Cadmium	<2-58	25
Chromium	15-84	44
Copper	25-75	48
Lead	5-40	8
Nickel	5-42	11
Zinc	10-70	30

Various authors have identified the importance of different elements for environmental reasons. Sandhu and Mills (1991) initiated an in depth study on Cd, Ni, Cr, and As, since they are on the USEPA's Priority List of Pollutants. They indicate the salts of these elements are highly toxic and Ni, Cr, and As are suspected carcinogens. Liem *et al.* (1983) studied the following elements because of their ecological interest: Cr, Co, Ni, Cu, Zn, As, Se, Mo, Cd, and Pb. Adriano *et al.* (1980) felt B was important to monitor since it is helpful to plants, but becomes toxic in higher concentrations. Theis and Gardner (1990) provided the ranges of composition for elements that make up less than one percent of the total. This list has been reproduced in Table 3 along with a summary of ranges from the reviewed literature. The major elements have been included, but are discussed in the following section. The literature reviewed for Table 3 include Block *et al.*, 1976; Theis and Wirth, 1977; Adriano *et al.*, 1980; Christensen *et al.*, 1982; Dlugi and Güsten, 1983; Roy *et al.*, 1984; Wadge *et al.*, 1986; Wong and Wong, 1989; Theis and Gardner, 1990; Sandhu and Mills, 1991.

The range of values for each element in Table 3 gives an indication of the variability of fly ash composition. EPRI (1992) reports a further breakdown of the concentration of elements according to the source of the feed coal. Generalizations are hard to make, especially regarding the minor or trace elements. More definition can be made about the presence of some of the major constituents, but as the following section (Major Constituent Composition) supports, the proportions can also vary significantly.

TABLE 3. Element Composition

Element	Range (ppm) (Theis and Gardner 1990)	Range (ppm) (cited literature)	No. of data pts.	Avg. (ppm)	Std. dev.
Al	--	59.7k-135k	9	102.2k	23k
As	6-1200	2.3-150	8	76.8	60
B	10-600	36-1.6k	8	1.24k	1.6k
Ba	100-1074	974-6.9k	3	3.39k	3.1k
Ca	--	14.8k-169.k	9	61.3k	64.2k
Cd	0.29-51	0.3-37.8	14	6.9	12.7
Ce	--	112-300	3	190.6	97.7
Cl	50-1000	13-50	2	31.5	26.2
Co	6.3-35	6.3-154.2	5	47.9	61
Cr	15-900	7.1-285	8	129	104.9
Cu	16-400	75-137	6	85.3	40.2
F	120-671	1.4-20	3	10.1	9.4
Fe	--	27.1k-129k	9	83.9	38.3
Hg	.04-10	0.1-22	5	4.5	9.8
I	--	1.3-4.2	3	2.7	1.5
K	--	5.6k-22.4k	3	11.8	9.2
Mg	--	15.1k-60.8k	3	31.2	25.7
Mn	100-1000	145-800	8	455	236
Mo	8.4-33	8.4-99	9	49.3	32.4
Na	--	1.5k-9.8k	4	4.1k	3.9k
Ni	1.8-13	1.8-253	11	97.7	90.9
P	--	100-8000	2	--	--
Pb	11-800	3.1-115.2	7	49.3	41.1
Rb	--	49-220	3	117.3	90.5
S	--	1k-25.1k	7	9.87k	8.14k
Sc	--	7.3-23	4	15.1	8.6
Se	6.9-760	1.2-24	11	11	6.5
Si	--	90k-243k	6	193k	58k
Sr	--	794-3.9k	3	1.86k	1.73k
Th	--	22-68	5	40.2	19.3
U	--	0.8-26	4	10.9	11.1
V	73-256	73-850	6	305.5	287
Zn	50-9000	14-500	6	135.6	195.4

2.4.1.2 Coal Verses Fly Ash

A discussion is necessary to identify the difference in composition between coal and fly ash. As we have noted, the surface area of the fly ash is enriched. This should be a strong indication that the chemical concentrations in coal will not necessarily help to predict the concentrations in the fly ash. Selective volatilization of some elements will result in an enrichment in the fly ash, while other elements will be depleted by the combustion (Block *et al.*, 1977). Spencer and Drake, 1987 report that metal concentrations on the surface of the ash can be two orders of magnitude greater than the parent coal. Elements where they found this to be true were Mo, Se, As, Cr, Zn, Cd, Pb, and Hg. All pertinent literature gives a unique list of elements that are enriched or depleted in the combustion process. For example, Roy *et al.* (1981) suggests the following elements have been found to be more concentrated in the fly ash than the parent coal: As, B, Br, Cl, Hg, I, In, Pb, Po, S, Sb, Se, and Zn; whereas the following have little or no enrichment: Al, Bi, Ca, Ce, Cs, Dy, Eu, Hf, K, La, Na, Nb, Nd, Sc, Si, Sm, Sn, Ta, Tb, Th, Ti, Y and Yb.

Studies by Block *et al.*, 1977 found changes in concentrations from coal to fly ash for the following elements (enrichment value shown in parentheses):

Na (+7x)	Al (+6.8x)	V (+6.2x)
Cr (+6.7x)	Mn (+11.2x)	Co (+7.5x)
As (+10x)	Se (+3x)	Hg (approx. equal)
Tb (+9.5x)	Si (+6.6x)	Pb (+2.8x)

A comparison of these lists reveals some conflicts. It should be remembered that the parent coals and plant processes were different for each of these studies. This is further evidence as to the importance of individual chemical analysis for fly ash samples.

2.4.2 Major Constituent Composition

Many studies have been performed to determine the possible constituent composition of fly ash. As noted previously, due to the high variability of fly ash, many different results are reported. A few authors have attempted to give an empirical formula (as mass percentages) for fly ash, but simultaneously give strong caution for their use:

- 1) SiO_2 -65.3; Al_2O_3 -25.2; Fe_2O_3 -3.4; CaO -3.1; Na_2O -1.6; TiO_2 -0.98; MgO -0.89; K_2O -0.89 (Western fly ash, study cited in Roy *et al.*, 1981),
- 2) SiO_2 -44; Al_2O_3 -23; Fe_2O_3 -11; CaO -8.2; C-4.0; MgO -2.7; K_2O -2.0; Na_2O -1.8; TiO_2 -1.3; P_2O_5 -0.8; MnO -0.1 (summary of data from various literature, Roy *et al.*, 1981), and
- 3) SiO_2 -50.4; Al_2O_3 -36.8; Fe_2O_3 -5.6; CaO -6.7 (Hollis *et al.*, 1988).

Empirical formula #2 is taken from a thorough review of data from approximately sixty publications. For more information on these publications see Roy *et al.* (1981). Table 4 provides a summary of their data. Characterization of fly ash in the laboratory will most likely be within the ranges noted.

TABLE 4. Range and Average Chemical Compositions

Constituent	Range (%)	No. of data	Average (%)	Standard deviation
SiO_2	2.19-68.1	58	44	13
Al_2O_3	3.39-39.4	60	23	6.5
Fe_2O_3	3.6-29.2	58	11	6.5
CaO	0.2-31.0	58	8.2	8.0
C	0.1-25.7	12	4.0	7.3
MgO	0.4-12.8	58	2.7	2.7
K_2O	0.2-8.1	49	2.0	1.8
Na_2O	0.2-8.0	50	1.8	2.0
SO_3	0.1-7.28	47	1.6	1.9
TiO_2	0.5-2.55	39	1.3	0.5
P_2O_5	0.08-6.0	34	0.8	1.7
MnO	0.02-0.24	14	0.1	0.1

Most data are in close agreement with the average or, at least, the ranges provided by Roy *et al.*'s (1981) report. Most of the literature only reported the

concentration percentages for the top four constituents since they account for a substantial portion of the total composition. A summary of more recent literature is provided in Table 5 (Golden, 1983; Markowski, 1985; Spencer and Drake, 1987; Hollis *et al.*, 1988; Goodwin, 1990; Ahmed, 1991). It can be seen that the average values agree with the data from Roy *et al.* (1981).

TABLE 5. Current Literature Range and Average Chemical Composition (1983 - 1991)

Constituent	Range (%)	No. of data	Average (%)	Standard deviation
SiO ₂	39.9-60	7	50.6	5.1
Al ₂ O ₃	16.7-36.8	7	25.5	6.1
Fe ₂ O ₃	3-12.41	7	7.9	3.2
CaO	1-24.3	7	9.1	7.5
MgO	0.3-4.6	4	2.1	1.8
K ₂ O	0.55	1	0.55	-
Na ₂ O	0.2-0.65	2	0.43	0.32
SO ₃	0.6-8.1	3	4.0	3.8
TiO ₂	0.7-1.0	2	0.85	0.21
P ₂ O ₅	1.2	1	1.2	-

The data in Tables 4 and 5 do not indicate the source or classification of the fly ash. It is evident from Ahmed's (1991) study that the classification of fly ash can provide some of the explanation for the range of the values seen in Table 4 and 5. The chemical composition reported by Ahmed (1991) for Class F (predominately eastern) and Class C (western) follow:

	<u>Class F</u>	<u>Class C</u>
SiO ₂	54.9 %	39.9 %
Al ₂ O ₃	25.8	16.7
Fe ₂ O ₃	6.9	5.8
CaO	8.7	24.3
MgO	1.8	4.6
SO ₃	0.6	3.3

EPRI (1992) also provides similar data. The most significant value is the high CaO content in Class C. As addressed previously, this contributes to the self-hardening characteristic of the Class C ash as opposed to the Class F.

The extent of composition identification is a direct result of the sensitivity of the analytical method. Golden (1983) suggests if the sensitivity were high enough, nearly all of the naturally occurring elements in the periodic table could be found. Analysis to this degree does not appear to be necessary. It is probably sufficient in most cases to know that the major constituents in descending order are SiO₂, Al₂O₃, Fe₂O₃, and CaO.

2.4.3 Mineralogy

Fly ash can be mineralogically divided into three major categories:

- 1) Amorphous Glass,
- 2) Mullite (3Al₂O₃·2SiO₂) - Quartz (SiO₂), and
- 3) Magnetic Spinel (includes magnetite (Fe₃O₄), hematite (Fe₂O₃), ferrite, and γ-Fe₂O₃)
(El-Mogazi *et al.*, 1988; Liem *et al.*, 1983).

Category two and three are crystalline phases. They collectively account for 25 to 30 percent of the composition (Liem *et al.*, 1983; Hartlén and Lundgren, 1983). Amorphous glass material predominates in most fly ash samples (Tazaki *et al.*, 1989). This is important since the glass portion gives fly ash its pozzolanic properties (EPRI, 1992). This essentially agrees with Cheremisinoff's (1988) mineralogical composition report with amorphous glass accounting for 50 to 90 percent of the fly ash matrix, mullite-quartz 0 to 20 percent and magnetic spinel 0 to 38 percent. Also small amounts of gypsum (CaSO₄·2H₂O) have been found in some western coal fly ash (Roy *et al.*, 1981). El-Mogazi *et al.* (1988) suggest that although the total percentage is small, particular attention should be given to the magnetic matrix of the ash because of its reactivity and potential for carrying and releasing toxic elements.

Other minerals from various sources are reported in the literature:

Roy et al. (1981): calcite (CaCO_3), anhydrite (CaSO_4), chlorite, goethite, fired illite and other clay, trace boron species,

Hartlén and Lundgren: calcium oxide (lime), calcite, calcium sulphate, calcium hydroxide (Ca(OH)_2),

Tazaki et al. (1989): sillimanite, trace TiO_2 , and

Mattigod et al. (1988): periclase, calcium ferrite.

Although the major phases are similar, the different minerals reported by the various authors are a reflection of the diversity of the fly ashes and their chemical compositions.

2.4.4 Organic Compounds

Although concentrations of inorganic compounds are far greater than organic compounds in fly ash, the organic content may be potentially hazardous. Some of the organic molecules present are known carcinogens and mutagens such as dimethyl and monomethyl sulfate and polycyclic hydrocarbons (PAH) dibenzofuran and benzo(a)pyrene (Roy et al., 1981). A study cited by Roy et al. (1981) found the total hydrocarbon content was approximately 9 ppm with low PAH concentrations ranging from 0.2 ppb to 37 ppb.

Theis and Gardner (1990) suggest that a large portion of the studies on specific organics have examined the respirable fraction of the stack samples (collected after the ash collection process). For example, research by Dlugi and Güsten (1983) investigated the hazard of PAH adsorbed on fly ash that is emitted from the stack. They concluded that PAHs are subject to long-range transport in the atmosphere. Although we do not know the total impact of organics in fly ash, it still may not be appropriate to accept the findings from stack emission studies.

A thorough study performed by Harrison et al. (1985) found a lower concentration of PAHs existed in the fly ash captured by the electrostatic precipitator (ESP) than in the stack. However, the ESP did have a greater organic concentration than the wet scrubber (WS), probably because the higher efficiency allows capture of particles that otherwise would escape into the atmosphere. An evaluation should be made on the fly ash with the greatest organic concentration. Since fly ash that is reused is not taken from the stack, fly ash from the ESP should be evaluated.

Harrison *et al.* (1985) state that the recovery of PAHs using modern methods is unsatisfactory (in their analysis PAHs with greater than four rings were lost), and better methods need to be investigated. This is confirmed in a study by Roy *et al.* (1984) where only one percent of the organic carbon was extracted into benzene for one sample and 0.1 percent for the other sample. Harrison *et al.* (1985) found that most of the aliphatic hydrocarbons were paraffins and terpenoids. Roy *et al.* (1984) found the majority of their organics to be paraffins (50%) and phenols (20%). A summary of the classes of organic compounds found in Harrison *et al.*'s (1985) study is provided in Table 6 (a complete summary of all organic compounds found in this reference).

TABLE 6. Concentrations of Organic Compound Classes in Extracts

CLASS	ESP FLY ASH - ORGANIC CONCENTRATION (ppb)
Aromatic Compounds	
one ring	2400
two ring	520
three ring	210
four ring	40
Nonaromatic Compounds	
Molecular Wt < 170	2100
Molecular Wt > 170	680
Total	6000

When the extracted compounds from Harrison *et al.*'s (1985) study were compared to the USEPA list of toxic water pollutants and toxic chemicals, only the PAHs and nitrogen-containing compounds were a concern. The PAH in largest concentration was naphthalene and its derivatives. The concentration in ESP fly ash equilibrated water was approximately 0.08 µg/L. Although the average PAH concentration in drinking water is 0.014 µg/L, some drinking water has a concentration as much as 1.4 µg/L (Harrison *et al.*, 1985). Although coal synfuels contain aromatic nitrogen containing compounds, none were found in ESP fly ash.

It is evident from the literature that the organic compound concentrations has not been heavily studied. Although it appears that the concentration of organics is well below regulatory "safe" limits, it remains a potential environmental hazard that should be investigated more thoroughly.

3.0 ENVIRONMENTAL CONCERNS

A researcher was quoted in 1976, "environmental hazards, real or purely speculative, must be solved or fly ash use may never reach its full potential" (Ahmed, 1991). Fifteen years have passed and it seems we are still in the same position. The public has not been convinced that fly ash is environmentally safe. A few organizations have committed resources to research encouraging the use of fly ash: Electric Power Research Institute (EPRI) and American Coal Ash Association (ACAA). However, most of the research so far has studied the feasibility of using fly ash in construction with regards to subjects such as strength and cost. It is evident with the increasing cost of proper disposal, the generators (power companies) must be the driving force behind the research. Presently fly ash is exempt from the Resource Conservation and Recovery Act (RCRA) hazardous waste disposal regulations. There has been enough concern about this exemption that it is necessary to have scientific evidence to verify that there is no environmental impact. Following is a summary of environmental concerns and the pertinent regulations for fly ash. The summary is based on the available research information published to date. The next chapter of this paper indicates specific concerns relevant to particular uses of fly ash.

3.1 Mobilization of Fly Ash Toxic Elements

The mobilization of toxic elements and subsequent contamination of the groundwater is an obvious environmental concern. There is an understanding of the elements that comprise the leachate (discussed previously in Section 2.3.3). The leachate elements were determined using standard extraction and solubility tests on pure fly ash samples. However, since reutilization techniques often involve mixing fly ash with other materials, these tests may not accurately reflect the technique's actual leachate formations. Testing under the actual fly ash placement conditions is needed; leaching may prove to be far less.

Golden (1983) suggests that mobilization of elements can be mitigated by either natural or engineered mechanisms. The natural mechanisms would include the buffering capacity of the soil, attenuation of trace metals in some soil types and organic matter, and low soil permeability.

1) The buffering capacity would influence the change of the pH of the fly ash up or down to provide an alkaline environment which will limit the solubility of most trace metals. As discussed previously, the least amount of metals are released when pH is approximately nine.

2) Clay and organic fractions of soil have a high affinity for some heavy metals and therefore can restrict their mobility.

3) The soil type can affect permeability. For example, clay soils have a low permeability which retards water movement.

The engineered mechanisms which Golden (1983) suggests to reduce mobilization are liner systems, leachate collection systems, fixation/stabilization of waste, site grading, waste cover, and surface water control.

One study performed by Usmen *et al.* (1988) investigated the effect of stabilization. They tested the leachate of several fly ash specimens stabilized with lime, cement or bentonite for Cd, Cr, Cu, Pb, Mn, Hg and Zn. They noted the most reliable results occurred for Cd. Table 7 Column 1 indicates the cadmium concentration in the initial leachate. Column 2 indicates the concentration in the leachate after one pore volume. Column 3 indicates the concentration in the final leachate after approximately two pore volumes (the parentheses indicate less reliable values).

TABLE 7. Leachate Analysis of Stabilized Fly Ash

Specimen	Cadmium Leachate Concentrations (mg/L)		
	1	2	3
Unstabilized	0.024	0.017	0.010
3% Lime, 7-Day Cure	0.020	0.007	0.007
3% Lime, 28-Day Cure	0.034	0.004	0.004
15% Cement, 7-Day Cure	0.016	0.006	0.005
15% Cement, 28-Day Cure	0.018	0.008	(0.004)
3% Lime, 2.5% Bentonite, 28-Day Cure	0.020	0.012	0.007
9% Lime, 2.5% Bentonite, 28-Day Cure	0.012	0.008	0.005
9% Cement, 10% Bentonite, 7-Day Cure	0.010	0.007	(0.006)
3% Cement, 2.5% Bentonite, 7-Day Cure	0.027	0.016	0.012

These results are somewhat promising. They indicate cadmium leaching can be reduced by some methods of stabilization. However, the results are not likely to be the same for all elements. The chromium test (not shown) indicated the addition of bentonite actually mobilized the chromium. Further tests of this type should be performed extensively for all leachable toxic elements.

The site grading, waste cover, and surface water limit the exposure of the fly ash to any precipitation, run-off, groundwater, etc. If the fly ash is "entombed" there is less chance of any leaching; therefore, contamination of groundwater. This is shown to be true in most existing construction uses of fly ash. Even if leachate was allowed to form, a liner could be used to protect groundwater from the leachate.

It is of some importance to note, although not all power plant ponds or disposal sites are properly lined, as of 1988, the National Priorities List included only one fly ash disposal site, Chisman Creek Superfund Site in Virginia (Williams and Okorn, 1988). However, some literature does report problems with groundwater contamination. Cherkauer (1980) studied a fly ash landfill in southeastern Wisconsin that was placed in direct contact with a shallow aquifer. Significant changes to the groundwater from sulfates, calcium and magnesium were reported, but they did not spread beyond 200 meters due to the site characteristics.

Murarka (1989) reported on two sites, an embankment in Illinois and a structural fill site in Minnesota. The embankment testing reported higher levels of sulfate and boron in the shallow groundwater with slight increases in As, Ba, Ca, Cl, Fe, Li, Mn, Mg, K, Na, and Sr. The elements dissipated as the distance and depth away from the embankment increased. The structural fill also showed increased levels of K, Na, Ca, Mg, SO₄, Cl, B, Fl, and Sr in shallow groundwater. Again the deep groundwater showed no effect from these elements, indicating vertical mixing and depth of penetration of the leachate was limited to a shallow groundwater zone (Murarka, 1989).

Simsiman *et al.* (1987) conducted a study of disposal ponds at a coal fired power plant in Wisconsin. Significant amounts of Na, SO₄, and B were released to the groundwater system. It was found that SO₄, Na and Mn were actually affecting the groundwater most, and B was only a concern if the groundwater was used for irrigation. The levels of As, Ba, Cu and Zn were below the enforcement standards.

The contamination of groundwater by fly ash leachate is a real concern. However, a direct correlation to the methods of fly ash reutilization and the effects on groundwater must be studied further. EPRI has started this research

on some projects (discussed in Chapter 4), but more investigation is needed to develop an adequate data base.

3.2 Biota Impact

The disposal or reutilization of fly ash could have a potential impact on the animal and plant life surrounding the area. Some research has been performed indicating what the effect might be.

3.2.1 Terrestrial Environment

3.2.1.1 Plants

Various studies have been performed to identify the consequences of fly ash contamination during plant growth. Fly ash can come into contact with vegetation through the use of soil amendments or agricultural growth on a soil-covered fly ash landfill. Fly ash can be very effective as a provider of certain essential trace nutrients to plants (B, Mg, Mo, S, and Zn (El-Mogazi *et al.*, 1988)). However, if the soil is already enriched with a particular element, the addition of more may prove to be toxic to the plant (Torrey, 1978b). Adriano *et al.* (1980) provided a list of elements that become enriched in agricultural plants grown on fly ash treated soil. Table 8 shows the elements with enrichment ratios greater than three. These elements do not always have a negative effect on the plant, but could be toxic to animals that eat the plants.

TABLE 8. Element Enrichment Ratios for Agricultural Plant Grown in Fly Ash

Element	Enrichment Ratio
Barium	3.5
Arsenic	3.8
Boron	4.8
Sulfur	5.3
Strontium	6.2
Selenium	8.3
Molybdenum	17.3

Adriano *et al.* (1980) provided a list of elements with potentially high toxicity: B, Cd, Co, Cr, Cu, F, Ni, Tl, and V. They found that although many trace elements in fly ash are considered potentially detrimental to plants, only B (at the levels found in plants) has been associated with any significant reductions in crop production. The B toxicity could last two to three years once B is integrated into the soil. Mo and Se are not toxic to plants, but repetitive ingestion of plants with high levels of these elements could induce psychological disorders in livestock (Adriano *et al.*, 1980).

The results of Adriano *et al.*'s (1980) experiment are based on fly ash amended soils, which normally contain less than ten percent fly ash by weight. The results of their experiment would likely be much higher if a higher concentration of fly ash was used. This could be the case for crops grown on soil covered fly ash landfills. Plants with deep roots could reach the fly ash at 100 percent concentration and accumulate much greater toxic concentrations (El-Mogazi *et al.*, 1988). This could be altered by providing a thicker soil covering on the landfill.

In addition to the elemental uptake in plants, the fly ash may restrict plants from growing at all or in a decreased state. The pozzolanic nature of fly ash could cause the soil to harden if the ratio is too high, thereby making it difficult to grow crops (Haas and Macak, 1985). The pH of the fly ash could either improve or deteriorate the crop growth. The pH affects the availability of some micronutrients, even inducing deficiencies. Additionally, an alkaline fly ash makes an acidic soil more conducive to growing crops, or makes a fertile soil too alkaline (or too acidic depending on the type of coal) (Adriano *et al.*, 1980).

3.2.1.2 Animals

Much of the research regarding the effect of fly ash on animals has been performed using plants grown in soil with fly ash. Adriano *et al.* (1980) provided a list of elements that have a potential high toxicity to animals: Be, Cd, F, Hg, Ni, Sb, Se, and Tl. The element that has repeatedly been found in animals from fly ash is Se.

Roy *et al.* (1981) reported in all studies that researched animals eating a partial fly ash diet or plants grown on fly ash, increased level of Se first in the blood, and eventually in various parts of the animals. However, no growth, strength, or pathological damage was noted.

Stoew sand *et al.* (1990) performed a study on rats fed rutabagas grown on a soil covered fly ash landfill. The covering was 45 to 60 cm thick. Their research found increased weight, food intake and Se level. This increased Se

level would indicate the plants were still able to absorb the Se from the fly ash even though presumably not in direct contact with it. They also note when clover grown on an uncapped fly ash landfill was fed to goats and sheep, high Se was found in their tissue and milk.

White *et al.* (1986) monitored American coot birds that were attracted to a particular ash pond as a resting and feeding site. No significant accumulation was noted in these birds; although, Cu did increase, but remained below the known effect level for birds.

It appears there is a definite impact on animals from fly ash, but it is not apparent yet how the increased Se affects animals. It should also be noted that animals need a certain amount of Se in their diet, and these plants could make up for a Se deficiency. However, too high of a concentration is likely not good either. El-Mogazi *et al.* (1988) concludes that short-term exposure does not cause changes in animals and humans, but the studies do not eliminate the possibility of damage due to long-term accumulation.

3.2.2 Aquatic Environment

Limited research has been done on the impact of fly ash on aquatic life. Adriano *et al.* (1980) suggested a list of elements in fly ash that have a potentially high toxicity to the aquatic biota: Be, Cd, Co, Cu, and Hg.

Research performed by Parker *et al.* (1983) exposed mussels in a salt water aquarium to fly ash which they ingested during their feeding process. They found increased levels of iron in the mussels, but no increase in the elements of most concern: Cd, Pb and Zn (Pb and Zn were listed as medium toxicity potential by Adriano *et al.* (1980)).

Cherry *et al.* (1987) found that fly ash was acutely toxic to blue-gill fish at 1360 mg/L total suspended solids (TSS). Whereas rainbow trout were highly sensitive to fly ash at TSS levels of 20.5 mg/L when the dissolved metals percentage of the TSS was 75 to 96 percent, but required a TSS level of 2,350 mg/L when the fly ash was first acid-leached to reduce the metal content. Both fish were more susceptible to acidic pHs, probably due to the higher percentage of dissolved metal available. The TSS generally contained Cd, Cr, Cu, Ni, Pb, and Zn.

If fly ash were to be reused in the aquatic environment (which is highly unlikely without extreme stabilization), more research would be necessary to ensure protection of aquatic life.

3.3 Microbial Impact

Microbial activity is necessary for normal organic matter decomposition and cycling of nutrients such as C, N, S, and P (Pichtel and Hayes, 1990). These processes are important to soil fertility and plant growth; therefore, any impact on them could effect plant growth. The information in this area is limited. However, it appears fly ash reduces microbial respiration due to either high pH or high trace metal concentration (El-Mogazi *et al.*, 1988).

Pichtel and Hayes (1990) performed a thorough investigation on the effect of fly ash on the microbial population and activity. The amount of fly ash added to the soil influenced the results. An addition of 5 percent (by dry weight) of fly ash to soil seemed to be beneficial to the microbes. The bacterial number increased slightly, probably due to the increase in nutrients. The addition of 10 and 20 percent fly ash markedly decreased the populations of bacteria, actinomycetes, and fungi by 57, 80, and 86 percent respectively. Respiration in each sample and at every time interval was drastically reduced compared to the control. This was reported to be a result of the toxic components in the fly ash. The control and 5 percent sample reached a stable respiration level after fourteen days. However, a slight increase was seen after 14 days in the 10 and 20 percent additions due to the indigenous microbes adapting to the contamination; the overall level was still significantly lower than the control.

Pichtel and Hayes (1990) do not indicate to what extent these effects damage soil fertility and plant growth. Microbial impact needs to be thoroughly investigated if fly ash amendments are to be used on a large scale, long-term project.

3.4 Potential Dangers of Handling Fly Ash

When handling fly ash it is likely to come into direct contact with external membranes such as skin and eyes, also the respiratory tract, and the alimentary canal (Roy *et al.*, 1981). There is no indication in the literature that there is a danger from external physical contact with fly ash. However, inhalation of fly ash is a potential hazard (Bree *et al.*, 1990).

Most respiratory research has involved the atmospheric emission from a coal-fired plant stack. Roy *et al.* (1981) reported on studies that tested the effect on animals from exposure to fly ash through air emissions. Increased levels of As (in the liver, kidney, and skin) and Fl (in the femurs) were found in two studies. Although the fly ash that can be reused differs from the fraction that becomes airborne, dust could be stirred up during the handling of fly ash and allow it to be introduced into the respiratory tract. Roy *et al.* (1981) suggest that since the ash

remains in the respiratory tract longer than the alimentary canal, the respiratory tract would be most vulnerable to the absorption of toxic metals.

There are few studies which examine the toxicity on the respiratory tract. Roy *et al.* (1981) indicates some authors concluded that exposure up to 0.05 mg/m³ was acceptable. They suggest this number is not based on completely adequate research.

Strauss (1984) and (1987) suggests dust control during disposal operations. The methods offered are as simple as spraying water or a chemical binder, and vegetating open areas.

Regardless of the application of fly ash, it must be handled by someone. The lack of literature seems to indicate this may not be a problem. However, a further review of this area should be done.

3.5 Regulations

In 1976, Congress passed the Resource Conservation and Recovery Act (RCRA). The purpose of this act was to "promote the protection of health and the environment and to conserve valuable material and energy resources" (RCRA, 1976). Presently, Subtitle C Section 3001 exempts coal fly ash from regulation as a hazardous waste. This has proved to be an advantageous position for the utility industry. The exemption encourages the utilization of the fly ash in lieu of disposal.

Unfortunately, there has been a public opinion problem primarily because Municipal Solid Waste (MSW) ash (also exempt) has frequently failed the USEPA EP toxicity test for Cd or Pb (100 percent of the fly ash in a study of 19 MSWs)(Theis and Gardner, 1990). Coal fly ash very rarely fails the EP toxicity test (the concentration limits allowed are listed in Table 9). The public has erroneously labeled both coal and MSW fly ash environmentally unsafe.

Regardless of some of the uncertainties, regulators have provided incentive programs that encourage the use of coal fly ash. In 1987 the Federal Highway Bill included a five percent increase in federal funding if coal fly ash was used in significant amounts for bridge or highway construction (Tyson, 1988; Turgeon, 1988). A variety of states have also passed incentives. For example, the Pennsylvania legislature amended its Solid Waste Management Act in 1987 to designate coal fly ash as a natural resource rather than a solid waste (Collins, 1988; Turgeon, 1988).

Fly ash is regulated by the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA) of 1977 which sets effluent limitation for discharge to surface waters. The EPA has a Primary Drinking Water Regulation (based on human health effects) and a Secondary Drinking Water Regulation (based on aesthetics, odor, taste, etc.) (Golden, 1983). Table 9 also provides a sample of the primary drinking water limits.

TABLE 9. Regulatory Limits for EP Toxicity Test and Drinking Water

Contaminant	EP Toxicity Limit (mg/L)	Drinking Water Limit (mg/L)
Arsenic	5.0	0.05
Barium	100.0	1.0
Cadmium	1.0	0.01
Chromium	5.0	0.05
Lead	5.0	0.05
Mercury	0.2	0.002
Nitrate (as N)	-	10
Selenium	1.0	0.01
Silver	5.0	0.05
Fluoride (Temp dep)	-	0.4 - 2.4
Endrin	0.02	0.0002
Lindane	0.4	0.004
Methoxychlor	10.0	0.1
Toxaphene	0.5	0.005
2,4-D	10.0	0.1
2,4,5-TP Silvex	1.0	0.01

(40 CFR 261.24, 1990; Golden, 1983; FDER, 1991)

4.0 OPTIONS FOR FLY ASH

The amount of fly ash produced in this country today cannot be ignored. Two options available for fly ash handling are disposal and reutilization. Current legislature encourages utilization of fly ash, but in practice this is still considered experimental. The two options are reviewed and the respective environmental concerns are addressed in this chapter.

4.1 Disposal

The literature does not address how long a disposal method should be monitored and controlled. However, the Swedish Coal-Health-Environment (KHM) Project has indicated that their assessment of the time perspective for the deposition of coal waste is 1000 years. This seems excessive when municipal landfills in the United States are monitored for thirty years (as long as no contamination is detected). Presently there are two methods, wet and dry, for disposal of coal-fired plant wastes. Often the selection of wet or dry disposal is a factor of the availability of water, accessibility of the disposal site, environmental regulations, and cost (Ruane *et al.*, 1983).

4.1.1 Wet Method

The most prevalent method of fly ash disposal has been by wet-sluicing to on-site ash ponds. Wet-sluicing has been the preferred method primarily because of the low relative cost. It is much less labor intensive because the fly ash is hydraulically conveyed to the ponds. Additionally, the ponds are near the power plant so essentially no shipping costs are involved.

Strauss (1987) describes the wet-sluicing process beginning with construction. The ash pond is a lined (or dual lined) area that has been either diked or excavated. The liner(s) is highly impermeable and normally manufactured from a polymer or rubber, or constructed of clay or a mixture of bottom and fly ash. The water run-on or runoff must be restricted by some method (ie. embankment). The sides of the pond are normally shallow sloped and stabilized with rip-rap or vegetation. Fly ash enters the pond and begins settling. The sedimentation process can be encouraged using certain design

methods. The supernatant liquid may be treated, discharged, recycled, evaporated or impounded in accordance with regulations and permits. The clarified ash water is discharged into a spillway and can be used to regulate the water level in the pond as necessary. The regulations and site conditions determine whether a leachate collection system and groundwater monitoring are required (most plants install monitoring wells regardless). Once the pond has reached a practical limit, it may be closed on site or dewatered, and the ash excavated allowing the pond to be reused.

There are negative aspects associated with wet disposal. Most noteworthy is the mobilization of toxic elements. The wet-sluicing places the fly ash in an environment where it is most dangerous. The mobilization could be controlled by ensuring an alkaline environment since, as noted previously, an acidic pH increases the mobilization. Although regulations today require ponds to be lined, complete containment is not guaranteed. This is driving the disposal preference toward a dry method. Besides the environmental implications, another factor influencing the choice is the amount of acreage necessary. As the fly ash generation has increased, the power plants have been running out of available land space. Wet-sluicing can take as much as 400 acres for the same amount of fly ash that a 40 to 50 acre dry landfill can handle (Strauss, 1987). The wet-sluicing method has begun to lose preference in light of increasing fly ash production, more stringent regulations, and the environmental ramifications.

However, with further research wet-sluicing could potentially be used to decrease the environmental impact in a reutilization project. If fly ash was allowed to pre-leach in a wet-sluicing pond, the elements available to leach later in the field would be reduced. EPRI (1986) performed analysis on fly ash samples at various stages of weathering. The elements B, As, and Se were nearly completely leached from the ash. However, Se and As were subsequently retained by fly ash through precipitation and adsorption. Approximately 50 percent of the total Sr, Ba, V, Mo, U, and Li in the fresh ash was mobilized and leached. Although not all elements can be pre-leached, any reduction is beneficial. If wet-sluicing were to be used in this capacity, the total containment and disposal of the leachate formed is very important. Since the primary concern for fly ash reutilization is the leachate that could potentially contaminate the groundwater, if handled properly, the mobilization of elements in a wet-sluicing environment could be advantageous. It should be reemphasized that further research is necessary in this area.

4.1.2 Dry Method

Dry method disposal takes place in a monofill constructed similar to a municipal landfill. As an example: a fly ash landfill constructed for the

Pennsylvania Electric Co. consists of a subbase (drainage zone), a liner, and a leachate collection zone with a protective cover layer (Strauss, 1987). Geotextile pads or coverings are suggested in between the layers to protect the liner and the drainage. The major concern in dry disposal is minimizing the production of leachate (Roy *et al.*, 1981). The site location can be very important to a successful disposal operation. The site should be above the groundwater table if possible to restrict the access of water to the fly ash. Efforts should be made to divert any surface water from the fill site. The better the fly ash is entombed, the less chance there is of contact with water which can trigger the release of toxic elements and form leachate.

The fly ash is either stored on site in silos or immediately transported to the landfill by trucks. The fly ash is spread in layers and compacted (Strauss, 1987). Since compaction of fly ash reduces the permeability, it is strongly suggested. If soils with low permeability are used to cover the fly ash, any water that does enter the landfill will follow the path of least resistance and be diverted away from the compacted fly ash.

Dust control may be a problem for dry disposal. Measures should be taken to reduce the amount of airborne fly ash. Light watering, minimal access to the area, and limited working areas can help this problem (Strauss, 1987). As with wet-sludging, groundwater monitoring is recommended to recognize contamination should it occur.

Fly ash dry disposal can be used advantageously to fill a mined quarry area to its original elevation. However, using a water filled quarry (especially one which penetrates the water table) is not recommended (Peffer, 1982). Another positive aspect to dry disposal is that the fly ash maintains its chemical properties. This would allow the material to be retrieved at a later date if it became desirable (Roy *et al.*, 1981). Although there are a number of advantages, dry disposal has become the preferred method primarily because of the leachate control.

4.2 Reutilization

In a survey performed by Ahmed (1991), out of forty two state highway agencies, 75.6 percent are using or experimenting with fly ash in a variety of highway applications. However, this is "just a drop in the bucket" with regards to quantity. Literature indicates only 20 percent of the fly ash produced in the United States is being reused (Sandhu and Mills, 1991). The American Coal Ash Association would like to reverse this ratio to a 80/20 reuse/disposal (Tyson, 1988). However, environmental uncertainty has been the limiting factor for fly ash reutilization. Various methods of utilizing fly ash have been studied, some

with more promising results than others. The following sections summarize the majority of possible uses studied to date.

4.2.1 Concrete Production

Fly ash is a pozzolan, a siliceous, or aluminous and siliceous, material which is not cementitious itself, but which, in finely divided form and in the presence of moisture, reacts with calcium hydroxide (lime) at ordinary temperatures to form cementitious products (EPRI, 1992; Collins, 1985; Torrey, 1978a). This property has made addition to concrete mix the most widely used form of fly ash recycling. Investigations by Ahmed (1991) found that cement and concrete production account for 10.7 percent of the total fly ash produced which is over half of the fly ash that is reused in the United States today.

There are two techniques for the mix design. In the first, fly ash replaces a portion of the cement. This is not usually allowed to exceed 20 percent replacement by cement weight (although this has been challenged by recent research (Sajadi and Head, 1988)). This method results in initially sluggish strength gain for the concrete (the final strength will ultimately be greater) and therefore curing time will be increased (Larsen, 1985). The second method uses fly ash as an admixture to the concrete mix (the amount added may vary for each mix design). This method produces a concrete of higher strength than that without fly ash. Roy *et al.* (1981) and Collins (1985) provided lists of advantages in addition to the increased strength. Fly ash provides a resistance to sulfate reaction with the hydrated lime and calcium aluminate; improved workability which reduces the water requirement resulting in lower bleeding which provides a more durable surface; reduction of permeability; better control of shrinkage; reduced heat of hydration; increased resistance against alkali aggregates; and reduced cost.

Larsen (1985) reports that in Florida until the Sunshine Skyway Bridge was built in the early 1980's, fly ash was permitted in pavements and non-stressed concrete in an amount not to exceed 20 percent of the cement content. Problems with concrete in the 1970's led Florida Department of Transportation to reduce the allowable amount to 10 percent, which effectively eliminated the use of fly ash in concrete. Now, FDOT's specifications allow fly ash in concrete at a 20 percent by weight replacement for concrete, although it is not evident how much fly ash is used in Florida (Larsen, 1985; Ahmed, 1991).

Extensive research has been performed verifying the feasibility and advantages of using fly ash in concrete. It is evident from the literature that nationally this is a widely accepted practice (Torrey, 1978a, Roy *et al.*, 1981; Larsen, 1985; Collins, 1985; Sajadi and Head, 1988; Tyson, 1988; Cheremisinoff,

1988; Goodwin, 1990; Ahmed, 1991) Unfortunately, there is no mention of any leachate studies, which would be the only concern after the concrete cures. Roy *et al.* (1981) indicates one author believes the potentially toxic trace elements are trapped or fixed within the concrete, but also confesses that no testing was performed to support this hypothesis. If the amount of fly ash use in this capacity is any indication, it appears there is not a great concern for future contamination. It would be prudent to investigate this application in order to confirm this mind set. However, it should be kept in mind, fly ash as a concrete additive is not the answer to the disposal problem. Collins (1985) claims if 100 pounds of fly ash were used in every cubic yard of concrete produced per year, this would only amount to about twelve million tons of fly ash used each year. Keep in mind that cement only accounts for approximately 15 percent by weight (about 600 lbs/yd³) of a cubic yard of concrete (about 4,000 lbs/yd³) (Merritt, 1983). One hundred pounds of fly ash per cubic yard of concrete would equate to 17 percent replacement of the cement. Nonetheless, it is evident that fly ash is beneficial to concrete and will continue to be used in this capacity.

4.2.2 Structural Fills/Embankments

Although the use of fly ash in concrete production has a majority of the market today, fly ash in structural fill has the potential of providing a large market for high volume recycling of fly ash. Currently, structural fills and embankments make up only 18 percent of the fly ash reutilization market (Ahmed, 1991). A survey performed by EPRI in 1984 revealed there were 33 embankments and 31 area fills in the United States and Canada constructed using fly ash (EPRI, 1992). Fly ash may be used as an effective soil stabilizer or as the entire fill. Many fill projects have been completed successfully and received high praise from the construction and structural aspect. However, since the environmental impacts have not been completely evaluated, construction project owners and contractors are somewhat tentative about increasing the use of fly ash in fills.

The possible formation of leachate and an associated contamination of the groundwater remain the greatest concern for fly ash used as a fill. One simple way to decrease this potential is to ensure the fill is above the groundwater table. Most highway embankments will meet this requirement. As discussed in Chapter Three, there are several techniques, such as a site grading, compaction, and surface water control, that can prevent this mobilization from happening. Some of the projects have tested these theories to restrict leaching. For example, Bacher (1990) reports on a project funded by EPRI called ASHRAMP that intended to document the design, construction, performance, and environmental characteristics associated with using compacted fly ash on highway embankment applications. The base and sides of the embankment used earthen borrow

material to entomb the fly ash and restrict infiltration of water. The fly ash was then compacted in 12 inch lifts to 95 percent of the maximum dry density (Delaware DOT specifications). The contractor on the project reported that the placement and resulting performance of the ash ramps were no different from traditional soil material ramps (under proper moisture conditions (Bacher, 1990)). Physically, the fly ash performed just as well as granular fill. Environmental monitoring also continued for two years and found that the fly ash fill placement has not measurably or detrimentally affected groundwater concentrations.

Martin *et al.* (1990) provide helpful hints from lessons learned during a construction project similar to the one described above. They indicate potential problems arise with wind erosion, surface-water erosion, dissolution in surface runoff, and dissolution in rainfall percolating to groundwater. Keeping the fly ash moist during the construction process will help with wind erosion and compaction. The other problems can be eliminated by methods such as entombment of the fly ash with a less permeable soil. The fly ash fill achieves required compaction with fewer passes of the vibratory roller, returning a cost savings to the contractor. Martin *et al.* (1990) reported that fly ash in their study was relatively innocuous from an environmental impact point of view, although only two sets of USEPA EP toxicity tests are reported.

Murarka (1989) reported extensive research on an embankment constructed in Waukegan, Illinois between 1970-72. Several core samples of the underlying soils in 1987 revealed no contamination or accumulation from the ash constituents. Plant tissues of grass and leaf plants showed accumulation and deficiencies of elements, but had no apparent visual symptoms of the changes. The groundwater downgradient of the embankment had increased levels of sulfate and boron, but the concentration quickly dissipated with distance away from the embankment. The testing process appeared to be adequate to support these conclusions. However, the embankment design is not described.

Turgeon (1988) described a construction project on which the Pennsylvania DOT accepted a contractor's value engineering proposal to use fly ash. This indicates a possible trend as contractors become more comfortable with the use of fly ash. The proposal included geotextile-aggregate blanket covered by a layer of borrow soil along the bottom of the entire fill area. This provides protection of the fly ash from water penetration. The contractor reported the necessity to keep the fly ash dry during the construction process to avoid installation problems. Turgeon (1988) was not able to report any test data analysis since monitoring would not be complete for two more years from the date of publish. However, results were reported by EPRI (1992) on the post two year construction monitoring which showed no adverse environmental effects and none are anticipated.

EPRI (1992) summarized a series of projects in their report. A project reported on was the testing of the Waukegan, Illinois embankment site. They confirm Murarka (1989) conclusions that the soil did not show any contamination, but the groundwater showed elevated levels of elements (B, Ca, Fe, F, K, Li, Mo, Si, SO₄⁻, and Sr) from fly ash. However, sulfate was the only analyte that had migrated more than 325 feet downgradient. Information is provided on three other projects. All were structurally successful, but none were monitored for environmental impacts. EPRI (1992) makes one other observation that does not seem to be addressed often. They reported that weathered fly ash will yield lower concentrations of soluble compounds than non-weathered ash (supported by EPRI (1986). They suggest this is because the elements have already leached out. Therefore, it would be beneficial to use ponded fly ash when available for construction until the environmental impacts are determined. They also address the possible need to obtain a permit from the state since some states consider the use of fly ash as fill material to be another means of disposal.

It is evident that structural fills are a very viable option for fly ash utilization. Contractors' and design engineers' unfamiliarity is an obstacle. The end-users need information on material properties and design details for construction with fly ash similar to those currently available for competing earthen materials. The environmental impacts are beginning to be monitored in the field. It will take continued field efforts to confirm the long term environmental safety of using fly ash.

4.2.3 Base and Subbase Material

Today fly ash as a road base material in a lime mix is relatively common, but the volume of fly ash used is not very high. Ahmed (1991) reports this option accounts for less than one percent of fly ash use. EPRI (1992) reports 74 subgrade stabilization projects, but only six pavement base course projects.

Collins (1985) reports on a DOE/DOT sponsored project for pozzolanic base course mixtures. The mix normally contains 2 to 6 percent lime or cement, 10 to 25 percent fly ash and 70 to 90 percent well-graded aggregate. Conventional paving, spreading and compaction equipment can be used. It is recommended the base be constructed before the winter months since the pozzolanic reaction all but ceases in temperatures below 40° F. The successful results are discussed. He states pozzolanic base course material using fly ash is environmentally acceptable, but no testing information is provided. Collins *et al.* (1988) provide a thorough paper on the design requirements for constructing a pozzolanic base, but again does not address any environmental issues.

EPRI (1992) provides a summary of information regarding subgrade stabilization and pavement base course. The strength and durability criteria applicable to lime or cement fly ash soil are discussed. The most often used criterion is ASTM C 593. The only environmental issues considered are those during construction: dust control, noise, traffic, and other similar factors. They indicate that no adverse problems (ie. leachate or groundwater impact) have been known to occur from subgrade stabilization (no data included). One project for pavement base course construction in Georgia had environmental monitoring performed. The reports indicate that environmental impact of the test sections has been negligible. They attribute this to the lack of water contact with the base course due to the wearing surface and drainage ditches. Another project constructed in Michigan is undergoing the long-term environmental monitoring sponsored by EPRI.

The literature indicates use of fly ash in subgrade is fairly common. However, environmental monitoring has been minimal. Because of the low fly ash volume in the subgrade mix designs, this application has not had a significant effect on the current volume of fly ash utilized. However, it could contribute since the miles of roads in the United States is quite extensive.

4.2.4 Other

4.2.4.1 Soil Amendment

Besides the use of fly ash for construction purposes, soil amendments are the most extensively studied reutilization option. Fly ash will change some soil properties. Mixed soil generally experiences a decreased bulk density, decreased moduli of rupture (index of the general strength), increased water holding capacities, and an increased hydraulic conductivity initially, which is later followed by a lower hydraulic conductivity (El-Mogazi *et al.*, 1988). Chang *et al.* (1977) found the increased water holding capacity did not necessarily increase the water available to vegetation. The fly ash has a cementing effect on the soil which contributes to the reduced hydraulic conductivity.

Different types of fly ash can change the pH of the soil either up or down. The pH influences the mobility of toxic elements (Boron) and many necessary nutrients. Therefore, the soil and fly ash pH could determine the available concentration of these elements (Cheremisinoff, 1988). Depending on the initial state of the soil, the results could be quite desirable.

The extent of the physical and chemical changes are dependent on the amount of fly ash added. Relevant studies have normally added between 5 and 50 percent fly ash. It has generally been found that more positive results are realized

at lower (5 percent) fly ash additions (Wong and Wong, 1989; Chang *et al.*, 1977; El-Mogazi *et al.*, 1988). Unfortunately, this small volume will contribute, but will not significantly alleviate, the disposal problem for fly ash.

4.2.4.2 Mineral Resource

Fly ash has been considered as a resource for a number of minerals such as Si, Al, Ca, S, P, Ti, Mg, Na, and Fe (Cheremisinoff, 1988). Most of the research to date has been most successful with Al. A 93 to 97 percent recovery of alumina from coal wastes have been reported (Torrey, 1978b). The various procedures that have been used for mineral recovery have been sulfuric acid extraction, artificial magnetite extraction, lime sintering and magnetic separation. It has been calculated that potentially 93 percent of fly ash could be utilized during the mineral recovery process, leaving seven percent as waste (Torrey, 1978a).

However, the variation in the feed coal and plant processes produce such a variety of fly ashes, one process would not produce satisfactory results for all ashes. Coal-fired power plants are located all over the United States. It would not be economically feasible to recover the minerals when the sources are so widely scattered (Torrey, 1978b). The primary reasons mineral recovery has not been heavily pursued is there are more economical ways to obtain minerals already in use today, and there are more economical uses for fly ash.

4.2.4.3 Underwater Construction

A series of projects have studied the possibility of forming stable blocks using fly ash and placing them in the ocean to act as a reef. A study performed by the State University of New York, Stony Brook, formed blocks by treating sludge and fly ash with additives (Parker *et al.*, 1983). A small amount of coal ash blocks were placed in the ocean with concrete blocks acting as a control. Eventually, a full scale reef consisting of 15,000 blocks weighing 500 tons was constructed and monitored. After one year in place, the reef formation had developed productive communities of reef organisms with no discernible differences between the test blocks and control blocks. The biomass have been tested for increased levels of trace elements since 1980. No increase has been found. The chemical composition of the blocks remained essentially the same. An increase of iron, lead, and magnesium concentrations occurred on the surfaces. Whereas, calcium levels decreased on the surface. As the blocks were exposed longer to the seawater, there was an increase in the density and compressive strength of the blocks with no signs of failure.

A project funded by power companies in New Jersey placed cement or lime stabilized coal ash blocks in the ocean and also found no structural or environmental problems (Bacher, 1990). In fact, they found the marine organisms thrived on the block reef.

The results of these projects were positive and further research in this area is suggested as a potential source for fly ash reutilization.

4.2.4.4 Preliminary Studies

In the push to find new methods of reusing fly ash, some unique projects have been attempted. Many do not yet appear to have follow-on projects, but they may be opening the door for further research and a viable alternative option.

Chu *et al.* (1991) investigated the possibility of using fixation as an option to restrict leaching of metals from contaminated soils at hazardous waste site remediation efforts. Although leaching is one of the main concerns for fly ash, Chu *et al.* (1991) studied whether fly ash could be used as a fixation material to reduce leaching. Combinations of water, cement, and fly ash were used, with the lowest arsenic concentration in leachate occurring when no cement was added and the water to fly ash ratio was 0.48. It is noted the best result sample was treated with 45 percent fly ash, but it is unclear what percent this indicates. The solution produced a rigid monolith and was successful in reducing the EP Toxicity and Toxicity Characteristic Leaching Procedure (TCLP) results for an arsenic containing soil from 22 mg/L to 0.09 mg/L. This demonstrates a 99 percent decrease in leaching. However, certain characteristics were not tested, such as the effect of the pH. Also, the costs were high compared to other alternatives.

Usmen *et al.* (1988) reported on research which evaluated the feasibility of using stabilized fly ash as a low permeable liner material. Because of the pozzolanic properties of fly ash, compaction, and the addition of other stabilizers such as lime, cement and bentonite, the permeability was able to be drastically reduced to approximately 1×10^{-6} cm/sec. However, regulations require 1×10^{-7} cm/sec for a liner. Leachate analyses are also preliminary.

Roy *et al.* (1981) report that fly ash can be used to control lake eutrophication. The fly ash absorbs phosphorous which can lower the productivity of an aquatic system. However, the fly ash may soon be covered by a layer of soil due to sedimentation and lose its effect.

As discussed previously, fly ash can be used to reclaim an area left damaged from strip mining. Various physical, chemical, and site characteristics

can change the outcome of a quarry filling (ie. alkaline groundwater raising the pH and immobilizing trace metals, or shallow groundwater more accessible for contamination) (Peffer, 1982; Adriano et al., 1980). Each site must be characterized separately to determine the feasibility of utilizing fly ash.

A semi-fluid slurry type application has been investigated by a few authors (Tyson, 1988; Torrey, 1978a; EPRI, 1992). Grouting application can be used to fill voids left during construction, or naturally occurring soil faults. The mix content can range from 20 to 90 percent fly ash by weight of the total grout mix. Type C is recommended since it has a self-hardening property which makes it beneficial for this application. This mix is advantageous since it can be pumped into remote areas and does not need compaction or vibration. The concerns with leaching into the groundwater are similar for this type of application.

Torrey (1978a) and Roy et al. (1981) suggest bricks as a possible option. Fly ash bricks could contain up to 75 percent fly ash and would require less heating and weigh less than clay bricks. However, no environmental testing is discussed by either of these authors. It is possible that radioactivity levels would be too high in a closed location should these bricks be used for building construction.

There are potentially many uses for fly ash, but it is important that the environmental impacts be thoroughly reviewed prior to its use. It is equally obvious that few applications have had thorough evaluation of potential environmental effects.

5.0 CONCLUSION

Fly ash is the fourth most abundant mineral resource, ranking behind coal, crushed stone, and sand and gravel (Collins, 1988). Yet, of the 80 million tons per year generated in the United States, over 60 million tons are discarded unused (Stoewsand *et al.*, 1990). With use of coal as an energy source continually on the rise, the disposal of fly ash will become more visible as a real issue in our country.

Although fly ash is presently exempt from RCRA handling requirements, some of the physical and chemical characteristics make fly ash potentially dangerous to the environment. The formation of leachate and consequential contamination of the groundwater is the greatest concern for the disposal or reuse of fly ash. Either method of handling suggests isolation from water is the best defense against leachate formation.

With this in mind the following recommendations are made. The use of fly ash as a structural fill or embankment has the most potential for high volume use and environmental safety. This option is still considered to be in the experimental stage. Continued research in the field is necessary to strengthen the confidence of the regulators, contractors, and end users for using fly ash safely, in a beneficial manner, and at a cost savings. Further field studies in pavement base course may also encourage use in this area.

The use of fly ash blocks for artificial reefs seems to contradict the recommendation to avoid water. However, initial research appears to be environmentally successful. Further studies in this area may prove to be beneficial to the fly ash generators. However, the demand for artificial reefs may not be high enough to make this method cost effective, but it may be a cheaper disposal option than wet-sluicing or dry landfilling.

Other areas of research that appear to be neglected should be initiated.

- 1) Most of the chemical testing is performed on the fly ash in its original state. Further testing should be performed in its reutilization state.
- 2) The existing literature does not adequately cover the potential dangers of handling fly ash during the construction processes. If there is no danger, this should be confirmed. If there are problems, control procedures should be developed.
- 3) Radioactivity appears not to be an issue. However, various measurements have exceeded the acceptable limit. This depends on the environment in which the fly ash exists, but further tests should determine the actual levels for specific ash sources and proper safety precautions or restrictions.

Appendix A provides a proposed protocol to cover research deficiencies found in the literature.

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APPENDIX A

PROPOSED PROTOCOL

The purpose of this protocol is to provide suggestions for research on the environmentally acceptable use of fly ash from coal-fired plants. The literature review provided a glimpse of many areas that require further research. The University of Florida can provide valuable research in several of these areas with adequate funding. The study of fly ash requires a very thorough approach. The phases of germane research outlined below are considered necessary to securing truly veritable new information.

Phase I: Characterization of Fly Ash

Fly ash is highly variable both physically and chemically. A complete characterization of various fly ashes should be made in order to provide comparative data. A thorough analysis would include fly ash from different source coals: anthracite, bituminous, subbituminous, and lignite. However, since this research is intended to investigate the possibility of using fly ash in Florida, the coal used in Florida would be adequate (most likely there are at least two different source coals used). Samples from plants with the same source coal, but different operating procedures should be analyzed to determine any differentiation. Two fly ash samples, one dry and one wet-sluiced, from the same plant should also be analyzed. A summary is provided for clarity.

Sample 1:	Plant #1 - Source Coal A, Operating Procedure 1, Dry
Sample 2:	Plant #2 - Source Coal A, Operating Procedure 2, Dry
Sample 3:	Plant #3 - Source Coal B, Operating Procedure 1, Dry
Sample 4:	Plant #4 - Source Coal B, Operating Procedure 2, Dry
Sample 5:	Plant #1 - Source Coal A, Operating Procedure 1, Wet-Sluiced
Sample 6:	Plant #3 - Source Coal B, Operating Procedure 1, Wet-Sluiced

This is the minimum number of samples recommended. The scope can be expanded, but at the expense of the field work becoming very extensive. Lengthy laboratory work is necessary to conduct this phase. The results will be used to identify correlations between certain properties and specific field reactions. The properties that should be determined for each sample are:

- Elemental Composition
- Major Constituent Composition
- Mineralogy
- Size Distribution
- Density
- Permeability/Hydraulic Conductivity
- pH
- Toxicity and Leachate Tests using either EP, TCLP or other methods suggested
- Radioactivity measurements

Phase II: Field Construction

A full scale project for various beneficial uses of fly ash will be developed. Most research performed to date tested fly ash alone in a laboratory setting. Most field testing has considered environmental monitoring to be of minimal concern (most projects neglected monitoring completely). The options that appear to have the greatest potential include fly ash in roadway and civil structure designs. Presently, fly ash is used primarily in concrete production; however, a greater volume of fly ash could be used if incorporated into subgrade material, structural fills, and embankments.

Each of the following fly ash utilization methods should be constructed using fly ash samples discussed in Phase I (provided that the analysis indicates that the fly ashes are significantly different). The University of Florida can not perform the actual construction, but will assure the sections are built to match the protocol. Assuming four of the six samples are used for the field construction, the number of test sections necessary is indicated in parentheses. For adequate analysis, each test section should be one quarter to one half mile long.

1) Concrete production: (32 test sections)

- Fly ash as a cement replacement - 10, 20, 30, 50 percent replacement by weight (20 percent is typical).
- Fly ash as an additive - 10, 40, 70, 90 percent equivalent cement weight added.
- monitor physical properties of the concrete.
- monitor (lab and field) quality of leachate from samples.

- 2) Subgrade material: (44 test sections)
 - Fly ash incorporation into the subgrade soil can be done in various mix proportions. If lime is added, ranges between 10 and 25 percent by weight of the fly ash are typical. For experimental purposes, a 10, 20, 30 and 50 percent by weight of fly ash/lime mix should be tested. If cement is used, fly ash is not often incorporated, but it may be beneficial. However, a study with a cement/fly ash percentages by weight (of the total mix) of 10/0, 10/10, 10/20 would be adequate.
 - Fly ash incorporation into the base course. For coarse aggregates, 10 - 20 percent by weight of the total mix is recommended. The study should include 10, 20, 30 , and 40 percent by weight.
- 3) Structural fill/ embankments: (12 test sections minimum)
Studies thus far show entombing fly ash is beneficial. Embankments and fill areas should be built with various construction designs. 100 percent fly ash with 2 foot cover on the sides and five foot cover on top and bottom; 50 percent fly ash/ 50 percent borrow material. Variation of the amount of cover can be made to find the minimum cover necessary (four different cover amounts with one sample are recommended). This information would be important for fly ash use in a small fill or embankment.

Phase III: Environmental Monitoring

The research that most benefits fly ash reutilization is monitoring field leachate. Each of the test sections constructed would need to be monitored for at least two years, but with a follow-up after five years. The actual design of the monitoring system will obviously be site specific. The monitoring should include tests for toxicity, groundwater contamination, and radioactivity. The following areas are necessary:

- 1) Groundwater collection and analysis:
Monitoring wells upgradient will establish a background level for each test section and wells downgradient will indicate any change in the groundwater.
- 2) Leachate collection and analysis:
A leachate collection system for each section should be installed during construction. Methods such as slotted pipes within the test area, liners, etc. can be used.
- 3) Surface water collection and analysis:
Drainage ditch collection. Although not as relevant as the groundwater, the surface water could provide information to supplement groundwater data.
- 4) Atmospheric conditions:
Monitoring the rainfall and temperature will provide information relevant to the leachate production. Air pollution monitoring for fugitive dust or particles.

Phase IV: Health Impact from Contact with Fly Ash

Develop experiments to determine potential dangers from handling fly ash during a reutilization project. Measurements for body contact, radioactive exposure levels, and inhalation should be researched. Evaluation of epidemiological effects on workers who are exposed to fly ash during work situations. Further areas may need to be defined.

Extensive environmental field research is acutely lacking to date. Sample sections of concrete, sub-base, base, and fill containing fly ash should be built and monitored. Different sources of fly ash will be used for comparative purposes. Efforts will be taken to provide a variety of site conditions. The more variations employed in the study, the more confidently the safe use of fly ash can be defined. However, the scope of the project can be significantly reduced by using one fly ash sample or selecting one utilization method. If a project reduction is necessary, the use of fly ash for structural fill or embankments will incorporate the highest volume of fly ash and therefore provide the utility industry a desirable substitute for disposal.